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**D3**

**(54) FIBER-REINFORCED RESIN MOLDING**

(11) 4-314740 (A) (43) 5.11.1992 (19) JP  
(21) Appl. No. 3-82328 (22) 15.4.1991  
(71) SEKISUI CHEM CO LTD (72) KATSUHIKO YAMAJI(1)  
(51) Int. Cl<sup>6</sup>. C08J5/06, C08J5/24

**PURPOSE:** To provide the title molding which can be easily produced in a short time, can be reinforced three-dimensionally, and can be easily deep-drawn.

**CONSTITUTION:** The title molding 1 is a composite of a resin material and a fibrous material and prepd. by bonding fibers oriented in three-dimensional directions to each other with a thermoplastic resin to give a fiber molding and filling voids of the fiber molding with a thermosetting resin.

**(54) POLYAMIDE FILM**

(11) 4-314741 (A) (43) 5.11.1992 (19) JP  
(21) Appl. No. 3-82153 (22) 15.4.1991  
(71) TORAY IND INC (72) HIDEYUKI UMETSU(2)  
(51) Int. Cl<sup>6</sup>. C08J5/18, C08L77/00

**PURPOSE:** To prevent the formation of pinholes and improve flexibility, transparency, and strengths by forming a compsn. comprising a polyamide and a specific polyetheresteramide elastomer into film.

**CONSTITUTION:** 10-80wt.% 6-12C lactam or aminocarboxylic acid, a polyoxytetramethylene glycol having a number-average mol.wt. of 600-2500, and an aliph., alicyclic, and/or arom. dicarboxylic acid in a molar ratio of OH of the glycol to COOH of the dicarboxylic acid of 0.9-1.1 are copolymerized to give a polyetheresteramide elastomer having a relative viscosity of 1.2-5.0. 99.5-91wt.% polyamide is melt mixed with 0.5-9wt.% the elastomer, formed into film, biaxially oriented successively, and thermally treated to give a 1-50 $\mu$ m-thick polyamide film.

ME 1238

Unexamined Patent Publication No. Hei 4-314741

Title of the Invention: Polyamide films

Japanese Patent Application No. Hei 3-82153

Application Date: April 15, 1991

Applicant: TORAY INDUSTRIES, INC.

### Specification

[Title of the Invention] Polyamide Films

#### [Claims]

A polyamide film comprising a composition in which (A) 99.5-91% by weight of a polyamide is blended with (B) 0.5-9% by weight of a polyether ester amide elastomer that is a copolymer of (i) a cyclic lactam or an amino carboxylic acid which have 6-12 carbon atoms, (ii) a polyoxytetramethylene glycol having a number-average molecular weight of 600-25,000 and (iii) at least one dicarboxylic acid selected from aliphatic dicarboxylic acids, alicyclic dicarboxylic acids and aromatic dicarboxylic acids.

#### [Detailed Description of the Invention]

##### [Industrial Field of the Invention]

The present invention is directed to polyamide films having excellent resistance to pinholes and flexibility.

##### [Prior Art]

Polyamide films have been used in a wide variety of fields, particularly in a food packaging field since they not only have good general mechanical properties, thermal and barrier properties but also have good impact and hardwearing properties, and resistance to pinholes,

which are important properties to wrapping materials. In recent years, since refrigeration techniques have been developed, polyamide films are often treated in low-temperature atmosphere after food is packaged therewith. Their resistance to pinholes and flexibility which are actually the most important among the above-mentioned properties are significantly temperature-dependent. For example, troubles such as ooze of packaged materials due to the generation of pinholes occur when polyamide films are used at temperatures lower than 10°C. The polyamide films in prior art are not necessarily satisfactory in use. As methods for overcoming the above problems of polyamide films, addition of polycaprolactams (Unexamined Patent Application (hereinafter referred to as "KOKAI") No. Hei 1-185363), addition of olefin ionomers (Examined Patent Application (hereinafter referred to as "KOKOKU") No. Hei 1-43624) and the like have been proposed.

In the meantime, as compositions comprising polyamides and polyether ester amide elastomers, compositions comprising 60-90% by weight of polyamides and 40-10% by weight of polyether ester amide elastomers of nylon 6/polyoxytetramethylene glycol (KOKAI No. Sho 63-278965) are known. These compositions can provide molded products having low water absorption properties and good dimensional stability.

[Problems to be Solved by the Invention]

However, the above methods could not improve sufficiently the resistance to pinholes in low-temperature atmosphere. If they could improving it, transparency and strength of films were sacrificed. Therefore, an object of the present invention is to improve resistance to pinholes of polyamide films while retaining their transparency and strength.

[Means of Solution of the Problems]

The present invention provides polyamide films comprising

compositions in which (A) 99.5-91% by weight of a polyamide is blended with (B) 0.5-9% by weight of a polyether ester amide elastomer that is a copolymer of (i) a cyclic lactam or an amino carboxylic acid which have 6-12 carbon atoms, (ii) a polyoxytetramethylene glycol having a number-average molecular weight of 600-25,000 and (iii) at least one dicarboxylic acid selected from aliphatic dicarboxylic acids, alicyclic dicarboxylic acids and aromatic dicarboxylic acids.

In the present invention, it is important to use in polyamide films compositions in which polyether ester amide elastomers composed of specific monomer units are blended in relatively small amounts with polyamide resins at given ratios and thereby the advantages of the present invention are obtained.

The present invention will be explained hereinafter in detail.

Examples of the polyamide used as (A) component in the present invention include, for example, ring opening polymers of cyclic lactam, polycondensates of aminocarboxylic acids, polycondensates of dicarboxylic acids with diamines and the like. Specific examples thereof include aliphatic polyamides such as nylon 6, nylon 4 · 6, nylon 6 · 6, nylon 6 · 10, nylon 11, nylon 12 and the like, aliphatic-aromatic polyamides such as poly(hexamethylene terephthalamide), poly(hexamethylene isophthalamide), poly(tetramethylene isophthalamide) and the like, copolymers and mixtures thereof. In particular, the preferred polyamides in the present invention are nylon 6 and nylon 6 · 6.

The polyether ester elastomer used as (B) component in the present invention is a uniformly-polymerized, tough and clear multi-block polymer having a hard segment of a ring opening polymer of a cyclic lactam or a polycondensate of an aminocarboxylic acid, and a soft segment of polyoxytertram thylene glycol. The relative viscosities of the polyether ester elastomers used in the present invention are

preferably 1:2 or higher in terms of toughness and resistance to pinholes and preferably lower than 5.0 in terms of the dispersibility in (A) component, more preferably in the range of 1.5-4.5, most preferably in the range of 1.5-4.0 as measured in orthochlorophenol (0.5 w/v%) at 25°C.

Examples of (i) component in the polyether ester amides include caprolactam, aminocarboxylic acids, aminododecanic acid, laurolactam, aminoundecanic acid and the like. The copolymerization amounts of them are not particularly limited, but in order to obtain tough elastomers, they are desirably used at the ratio of 10-80% by weight, preferably 15-75% by weight, more preferably 20-70% by weight. Furthermore, the copolymerization amount of (i) component is suitably selected depending on the physical properties of elastomers to be obtained and the molecular weight of polyoxytetramethylene glycol to be used. The number-average molecular weights of elastomers having carboxyl groups at both ends which are composed of hard segments of (i) component and (ii) the dicarboxylic acid are preferably 500-5,000. If they are smaller than 500, the cohesive powers of the hard domains are reduced and thereby the mechanical strengths of the elastomers are lowered. If they are larger than 5,000, the polymerization may be difficult.

The number-average molecular weight of (ii) the polyoxymethylene glycol in the polyether ester amide elastomers should be in the range of 600-2,500 and the copolymerization amount thereof are not particularly limited and suitably selected depending on required properties of the elastomers such as low-temperature physical properties, heat and weathering resistances, and the like. If the number-average molecular weight of the polyoxymethylene glycol is smaller than 600, problems occur that the melting points of elastomers to be obtained become lower and that physical properties thereof are

not satisfactory. If the number-average molecular weight of the polyoxymethylene glycol exceeds 2.500, the number of polymerizable sites becomes smaller and thereby it is difficult to control polymerization systems.

The dicarboxylic acid as (iii) component in the polyether ester amide elastomers is not particularly limited and the OH/COOH molar ratio to the polytetramethylene glycol is preferably 0.9-1.1, more preferably 0.9-1.05, most preferably 0.9-1.0 in order not to reduce mechanical properties due to higher or lower molecular weights of elastomers to be obtained.

As the dicarboxylic acids, at least one selected from aliphatic dicarboxylic acids, alicyclic dicarboxylic acids and aromatic dicarboxylic acids can be used and the number of carbon atoms therein is preferably in the range of 4-20. Examples thereof include aliphatic dicarboxylic acids such as adipic acid, sebacic acid, pimelic acid, suberic acid, azelaic acid, dodecane dicarboxylic acid and the like, alicyclic dicarboxylic acids such as cyclohexane dicarboxylic acid, decalin dicarboxylic acid and the like, and aromatic dicarboxylic acids such as isophthalic acid, terephthalic acid and naphthalene dicarboxylic acid.

In the present invention, methods of preparing the polyether ester amide elastomer used as (B) component are not particularly limited and usual and known methods (Examined Patent Publication (hereinafter referred to as "KOKOKU") Nos. Sho 56-45419, Sho 58-11459, Sho 57-24808 and Unexamined Patent Publication (hereinafter referred to as "KOKAI") No. Sho 58-21095) can be used.

The blending ratio of (A) component of the polyamide to (B) component of the polyether ester amide elastomer should be in the range in which the amount of (A) component is 99.5-91% by weight and the

amount of (B) component is 0.5-9% by weight, preferably that of (A) component is 99-93% by weight and that of (B) component is 1-7% by weight, based on the total weight of components (A) and (B). If the amount of component (B) is less than 0.5% by weight, improvement in resistance to pinholes is not satisfactory. If the amount of component (B) is more than 9% by weight, improvement in resistance to pinholes is satisfactory but film strength and transparency are reduced.

The compositions used in the present invention are processed preferably by melt-blending as follows:

The compositions are melt-blended with a Banbury mixer, a mixing roller, a single- or double-screw extruders and the like to obtain pellets of the mixtures. The pellets of the mixtures are re-melted and films are formed therefrom by T-die method, inflation method and the like to obtain unoriented films. Alternatively, components (A) and (B) are melt-blended with an extruder and films are formed by the methods described above to obtain unoriented films. Subsequently, the unoriented films are oriented in at least one direction. In usual, successive biaxial stretching techniques in which longitudinal and traverse stretchings are conducted in this order are preferably used in terms of productivity. Of course, unoriented or simultaneously and biaxially oriented films can be used and the stretching properties thereof are very good. In addition, heat treatments after the orientation are preferably performed in order to retain dimensional stability and resistance to hot water, and stretch or unstretch heat treatments are effective.

The thicknesses of the films thus obtained are 1-50  $\mu\text{m}$ , preferably 1-4  $\mu\text{m}$ , most preferably 5-40  $\mu\text{m}$  but are not particularly limited in the above ranges.

The resistance to pinholes depends on the thickness of the film



and it becomes inferior as the the film becomes thicker. If the thickness of the film exceeds 50  $\mu\text{m}$ , desired characteristic values can not obtained even if the polyether ester amide elastomers are added.

If the thickness of the film is less than 1  $\mu\text{m}$ , the film can not be used as a strength-retaining material. The films of the present invention are valuable even if used alone. In addition, they can be used laminating and blending with other thermoplastic resins. Many properties such as gas-barrier properties, tear propagation strength, heat resistance and the like can be improved and the value of the films becomes greater. Preferred examples of the other resins include EVOH, polyolefins, polyesters and the like. EVOH is usually used for blending and laminating and polyolefins and polyesters are used for laminating. The properties of the laminated films vary depending on the kind of the thermoplastic reins used for laminating. For example, if the films are laminated with EVOH, the oxygen permeability can be significantly reduced. If the films are laminated with the polyester resins, the heat resistance can be improved.

Furthermore, to the films of the present invention, other components such as heat stabilizers, crystallization nucleators, anti-oxidizing agents, lubricants, fillers, plasticizers and the like may be added unless they do not impair the properties of the films.

[Examples]

The present invention will be explained in more detail with reference to the following examples. These examples are not intended to limit the scope of the present invention without departing from the scope of the present invention. The properties of films were evaluated according to measurement methods described below.

(1) Resistance to pinholes (Repeated Flexing Fatigue Test)

According to Method 2017 in Fed. Test. Method Std. No. 101C shown in MIL-B-131F, films are bended repeatedly 1000 times with a Gerbo tester at 0°C and then the number of pinholes generated in the films is counted.

(2) Transparency (Haze value)

Haze tests are carried out according to JIS-K-6714 method.

The results of these tests are shown in Table 1.

(Working Example 1)

To nylon 6 (TORAY INDUSTRIES, INC., "AMILAM" CM1010), a copolymer (polyether ester amide elastomer) of nylon 6 with polyoxytetramethylene glycol having a number-average molecular weight of 650 at a ratio of 45/55 expressed in % by weight was added in an amount of 9% by weight. The mixture was melt-extruded with a double-screw extruder at 260°C and subsequently with a T die, and cooled on a drum at 30°C to obtain unoriented films having a thickness of 180  $\mu$ m. Then, the films were oriented simultaneously and biaxially 3.4 fold in the longitudinal direction and 3.5 fold in the traverse direction at 80 °C to obtain films having good resistance to pinholes in a thickness of 15  $\mu$ m.

(Working Example 2)

The same procedure as Working Example 1 was repeated except that to nylon 6 (TORAY INDUSTRIES, INC., "AMILAM" CM1010), a copolymer (polyether ester amide elastomer) of nylon 6 with polyoxytetramethylene glycol having a number-average molecular weight of 800 at a ratio of 30/70 expressed in % by weight was added in an amount of 5% by weight to obtain films having good resistance to pinholes.

(Working Example 3)

The same procedure as Working Example 1 was repeated except that to nylon 6 (TORAY INDUSTRIES, INC., "AMILAM" CM1010), a copolymer

(polyether ester amide elastomer) of nylon 12 with polyoxytetramethylene glycol having a number-average molecular weight of 650 at a ratio of 30/70 expressed in % by weight was added in an amount of 4% by weight to obtain films having good resistance to pinholes.

(Comparative Example 1)

The resistance to pinholes of films of nylon 6 (TORAY INDUSTRIES, INC., "AMILAM" CM1010) alone were inferior to that of the films of the present invention.

(Comparative Examples 2 and 3)

Films that had the same compositions used in Working Examples but in which the polyether ester amide elastomers were added to the polyamide in amounts out of the range of the present invention were prepared and evaluated. Films prepared in Comparative Example 2 had unimproved resistance to pinholes and films prepared in Comparative Example 3 had good resistance to pinholes but had inferior transparency.

Table 1

|                       | Polyamide | Polyether ester amide elastomer |                      | Thickness of Films ( $\mu$ m) |
|-----------------------|-----------|---------------------------------|----------------------|-------------------------------|
|                       |           | Composition Ratio (% by weight) | Amount (% by weight) |                               |
| Working Example 1     | Nylon 6   | Nylon6/PTMG =45/55              | 9                    | 15                            |
| 2                     | Nylon 6   | Nylon6/PTMG =30/70              | 5                    | 15                            |
| 3                     | Nylon 6   | Nylon12/PTMG =30/70             | 4                    | 15                            |
| Comparative Example 1 | Nylon 6   | -                               | -                    | 15                            |
| 2                     | Nylon 6   | Nylon6/PTMG =45/55              | 0.05                 | 15                            |
| 3                     | Nylon 6   | Nylon6/PTMG =30/70              | 22                   | 15                            |

Table 1 (Continued)

|                          | The Number of<br>pinholes<br>at 0°C | Transparency<br>Haze Value<br>(%) |
|--------------------------|-------------------------------------|-----------------------------------|
| Working<br>Example 1     | 3                                   | 6.0                               |
| 2                        | 4                                   | 5.0                               |
| 3                        | 4                                   | 5.1                               |
| Comparative<br>Example 1 | 25                                  | 3.5                               |
| 2                        | 24                                  | 3.6                               |
| 3                        | 3                                   | 16                                |

Note: "PTMG" shown in Table 1 means polyoxytetramethylene glycol.

[Advantages of the Invention]

According to the present invention, by adding the polyether ester amide elastomers to the polyamides in given amounts, it makes possible to improve resistance to pinholes at low temperatures, which is important to polyamide films, while retaining transparency of the films.

In addition, according to the present invention, the use of polyamide films at low temperatures can be greatly broadened.

[Abstract of the disclosure]

[Subject Matter] A polyamide film comprising a composition in which (A) 99.5-91% by weight of a polyamide is blended with (B) 0.5-9% by weight of a polyether ester amide elastomer that is a copolymer of (i) a cyclic lactam or an amino carboxylic acid which have 6-12 carbon atoms, (ii) a polyoxytetramethylene glycol having a number-average molecular weight of 600-25,000 and (iii) at least one dicarboxylic acid selected from aliphatic dicarboxylic acids, alicyclic dicarboxylic acids and aromatic dicarboxylic acids.

[Advantages of the Invention] According to the present invention, by adding the polyether ester amide elastomers to the polyamides in given amounts, it makes possible to improve resistance to pinholes at low temperatures, which is important to polyamide films, while retaining transparency of the films. In addition, according to the present invention, the use of polyamide films at low temperatures can be greatly broadened.